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(71) Applicant: COBARR S.p.A.
Via Anticolana Km 1
I-03012 Anagni Frosinone(IT)

(72) Inventor: Al-Ghatta, Hussain-Ali-Kashif
Via Diaz
I-03014 Fiuggi (Frosinone)(IT)

(74) Representative: Rambelli, Paolo et al
Jacobacci-Casetta & Perani S.p.A. Via Alfieri 17
I-10121 Torino(IT)

(54) A method for recycling PET beverage bottles.

(57) A method for recycling PET beverage bottles comprises the removal of the contaminants with the use of supercritical carbon dioxide.

A method for recycling PET beverage bottles

The present invention relates to a method for recycling polymer materials based on polyethyleneterephthalate and polyethyleneterephthalate copolymers, particularly for recycling polyethyleneterephthalate beverage bottles.

The general known method comprises the step of chopping the bottles into small pieces and of separating the PET material from aluminium cap, adhesively bounded paper and polyethylene foot or cup using float-sink techniques or air separation.

Until now, the PET resins are not suitable for reuse as beverage containers because of possible contamination which could interfere with blow molding or with cleanliness required for a food package. Such contamination may derive from an improper use of the bottles in the household to contain liquids (aceton, acetic acid etc.) which diffuse in the bottle walls.

The object of the present invention is to provide a method for recycling PET resins which makes them adapted to be used for food applications.

According to the invention, this object is achieved by virtue of the fact that the materials are treated in an atmosphere containing carbon dioxide under supercritical conditions.

When recycled PET resins in the forms of crushed bottles are submitted to a supercritical fluid extraction using an atmosphere containing carbon dioxide, the supercritical fluid penetrates the surface of the crushed bottles and extracts the contaminants and impurities out of it.

The effect of CO_2 is surprising if one thinks that PET resins contain polar groups (carboxylic, OH and ester groups) and that these polar groups show great affinity to polar impurities such as fungicides and insecticides. A man skilled in the art would use polar solvent gases such as halogenated hydrocarbons to extract polar impurities. Applicant, however, has discovered that carbon dioxide, a relatively non-polar solvent gas, is effective in removing polar impurities from PET resins under supercritical conditions.

A mixture of supercritical CO_2 and other supercritical fluids, especially water vapor, could be also used for the purification of the recycled PET.

In order to obtain the best results in the extraction of the impurities, pressures greater than 50 bars and temperatures between 31° and 245° C are preferred.

The invention would be better understood with the aid of the following examples, whose contents should not be understood as limiting of the scope of the present invention.

The impurities contents of the examples have been measured by the head space gas chromatographic method described in EP-A-86830340.5.

EXAMPLE 1

20 kg of recycled PET crushed bottles, contaminated with aceton to a level of 10.500 ppm, were treated in an autoclave containing CO_2 and 2% by weight of water vapour at 100 bars for 3 hours at an average temperature of 120° C. The gas chromatograph test of the powdered PET after the treatment shows no aceton. The intrinsic viscosity of PET crushed bottles before and after the treatment was respectively 0,787 and 0,778 dl/g.

EXAMPLE 2

20 kg of recycled PET, contaminated with acetic acid to a level of 20100 ppm, were treated in an autoclave containing CO_2 at 250 bars for 2 hours at an average temperature of 130° C.

The gas chromatographic test shows a content of 3 ppm of acetic acid. There is no decrease in the intrinsic viscosity of the polymer before and after the treatment.

EXAMPLE 3

20 kg of recycled PET, contaminated with carbon tetrachloride to a level of 10250 ppm, were treated in an autoclave containing CO_2 at 280 bars for 5 hours at an average temperature of 150° C.

The gas chromatographic test of the powdered PET after the treatment shows no carbon tetrachloride. There is no decrease in the intrinsic viscosity.

EXAMPLE 4

200 kg of recycled PET, contaminated with trichloroethane to a level of 500 ppm, were treated in an autoclave containing CO_2 at 150 bars for 3 hours at an average temperature of 145° C. The G.C. test shows a content of

2,3 ppm of trichloroethane. There is no decrease of intrinsic viscosity.

EXAMPLE 5

200 kg of recycled PET, contaminated with methylbenzoate to a level of 220 ppm, were treated in an autoclave containing CO_2 at 165 bars for 5 hours at an average temperature of 155° C.

The G.C. test shows a content of 1,2 ppm of methylbenzoate. There is no decrease of intrinsic viscosity.

Other tests were carried out filling PET bottles with fungicides, insecticides, deodorants, naphta and leaving them on a shelf for one week.

Then the bottles were emptied, crushed and treated according to the present invention. From the recycled PET, new bottles were obtained. These new PET bottles were filled with water that, after a storage of 3 months in the bottles at 40° C has shown no appreciable taste, and it was not possible to detect any of the above impurities in the water.

EXAMPLE 6

Recycled PET polluted with the products identified in the following table were treated in autoclave containing humified CO_2 (0,5% H_2O) at 130 bars for three hours at an average temperature of 80° C. The test was repeated for each class of pollutant.

For the analysis of the samples, after and before the treatment with CO_2, the polluted PET has been extracted for 24 hours with n-hexane. The effectiveness of the supercritical CO_2 treatment has been determined by gas chromatographic mass spectrometer analysis of the extraction solution. A Perkin Elmer Gas Chromatograph series 8420 with capillary column legth 12m and internal diameter 0,2mm (phase OV1 - Ion Trap Detector - Mass Spectrometer) coupled with NBS/EPA Library of 42.000 Mass Spectra has been used. The results are shown in the following table.

Analytical results of SFE treatments for decontamination process of recycled PET.				
Test No.	Pollution	Contaminant	Before SFE treatment ppm	After SFE treatment ppm
6.1	A FUNGICIDE	CAPTAN	5 ppm	ABSENT
		DINOCAP	5 ppm	ABSENT
		VINCLOZOLIN	151	
6.2.	B INSECTICIDE	BENDIOCARB	13	ABSENT
		MALATHION	1 ppm	ABSENT
6.3	C HERBICIDE	BENTAZON	139	ABSENT
		METRIBUZIN	5 ppm	ABSENT
6.4.	F DRY CLEAN FLUID	ETYLENE TRICHLORO	19.4	ABSENT

EXAMPLE 7

Recycled PET polluted with household insecticide (type COMBO commercialized by BASF AGRITALIA S.p.A.) were treated in autoclave containing Co_2 at 100 bars for four hours. For the analysis of the sample

the same instrumentation of example 6 has been used. Only a qualitative analysis by NBS/EPA Library has been obtained, on which are based the identifications of all the peaks displayed in chromatogram 1 enclosed. The peaks are due to the presence of several compounds which have been identified as the following normal home-insecticide content:

Peak 1: DDT PP' 1,1 BIS (4 CHLOROPHENYL) - 2,2,2 -TRICHLOROETHANE

Peak 2: DDT 1,1 BIS (4 CHLOROPHENYL) - 2,2,2 -TRICHLOROETHANE

Peak 3: P.B.O. PHENOL, 4 (5,6,7,8 TETRAHYDRO - 1,3 -DIOXOLO (4,5,6) ISOQUINOLIN-S-YL) HET

Peak 4: NEOPYNAMIN

Peak 5: METOXYCHLOR (2,2- BIS (4-METHOXYPHENYL) - 1,1,1 - TRICHLOROETHANE)

The sample treated with supercritical CO_2 shows the chromatogram 2 enclosed. No signal from pesticides is detectable using a higher sensitive monitoring (chromatograms 3.1, 3.2, 3.3 enclosed) instead of the general purpose investigation technique used for the chromatograms 1 and 2.

Claims

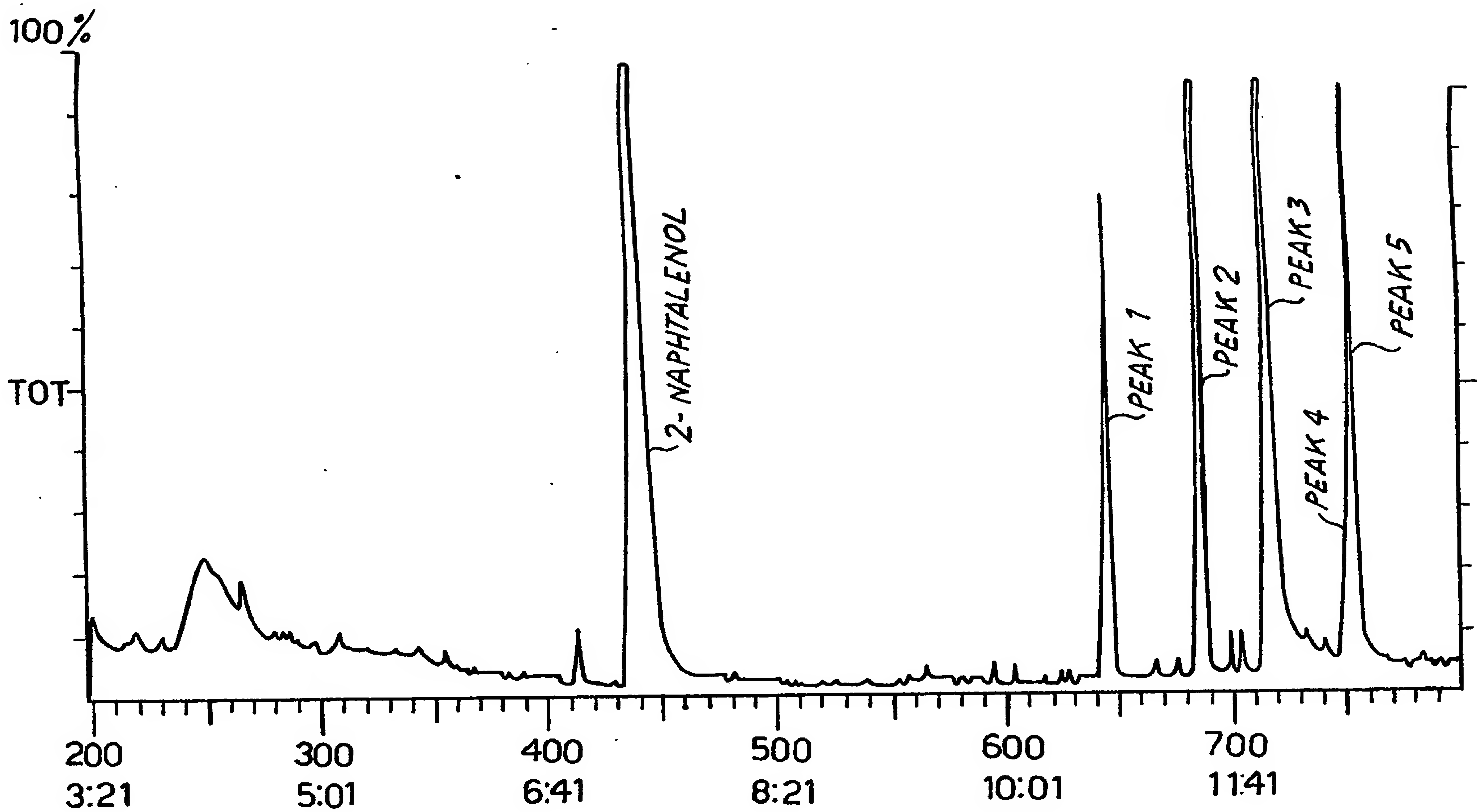
1. Method for recycling polymer materials based on polyethyleneterephthalate and polyethyleneterephthalate copolymers, particularly for recycling polyethyleneterephthalate beverage bottles, wherein the materials are treated in an atmosphere containing carbon dioxide under supercritical conditions.

2. A method according to claim 1, wherein the treatment is carried out at a pressure greater than 50 bars.

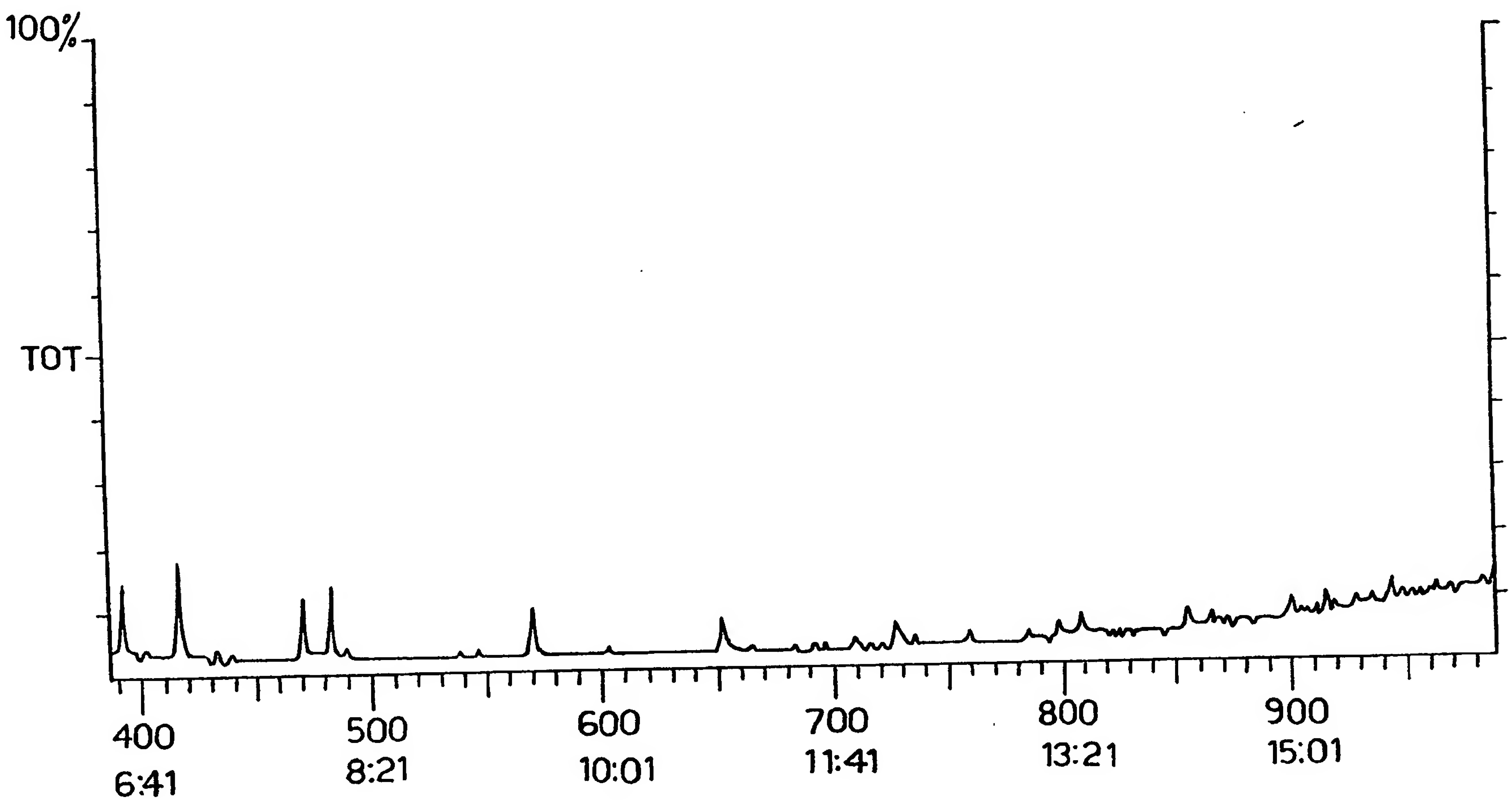
3. A method according to claim 1, wherein the treatment is carried out at a temperature between 31 °C and 245 °C.

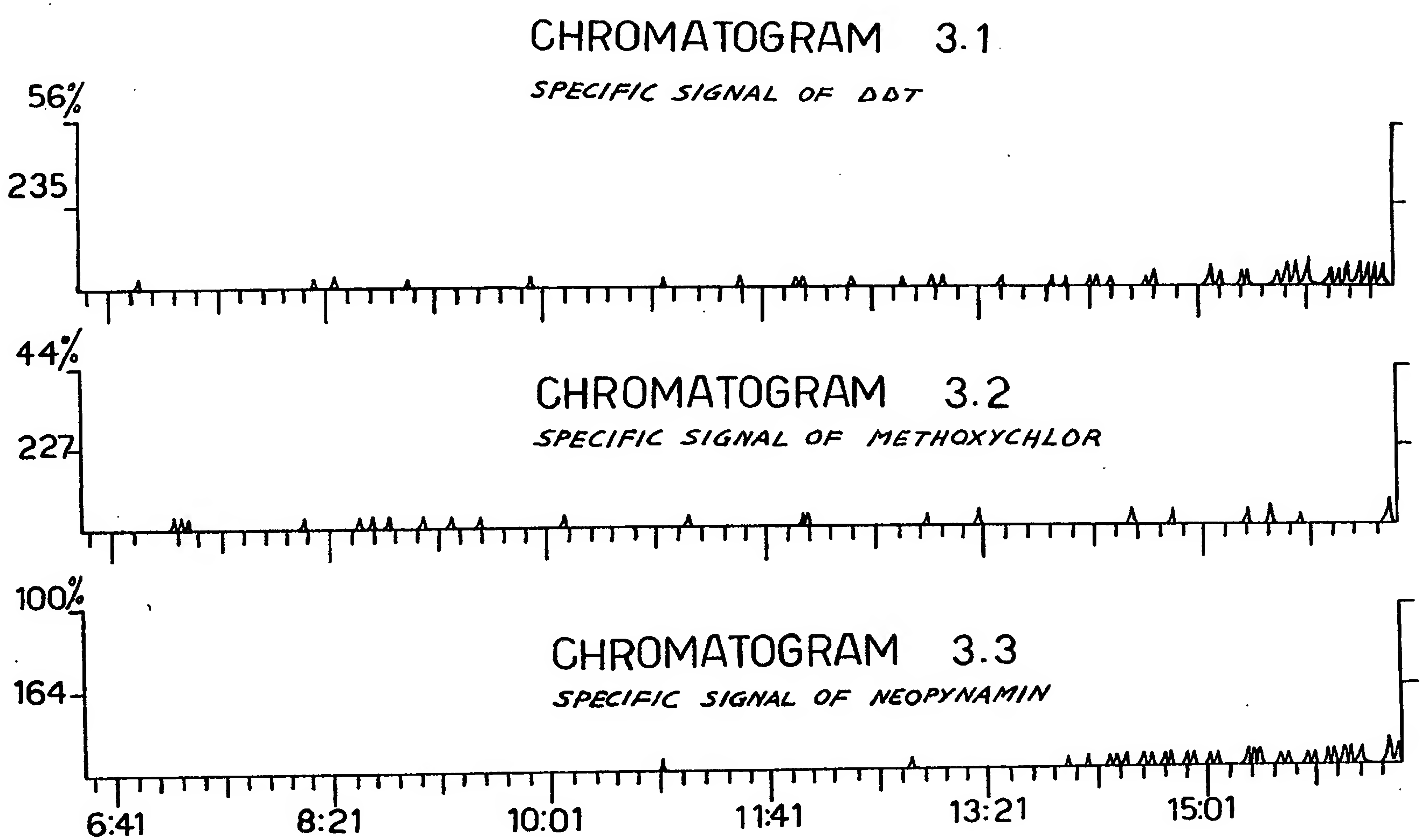
4. A method according to claim 1, wherein the atmosphere in which the materials are treated contains water vapour in addition to the supercritical carbon dioxide.

CHROMATOGRAM 1



CHROMATOGRAM 2




CHROMATOGRAM 3.1
SPECIFIC SIGNAL OF DDT
56%
235
CHROMATOGRAM 3.2
SPECIFIC SIGNAL OF METHOXYCHLOR
44%
227
CHROMATOGRAM 3.3
SPECIFIC SIGNAL OF NEOPYNAMIN
100%
164
6:41
8:21
10:01
11:41
13:21
15:01